

## TRANSLATION

(19) JAPANESE PATENT OFFICE (JP)

### (12) **UNEXAMINED PATENT APPLICATION (A)**

- 5 (11) Unexamined Patent Application KOKAI No. Hei 3-66725  
(43) Date of Publication: March 22, 1991  
(51) Int. Cl.<sup>3</sup> ID.No. Intraoffice filing no.  
C 08 G 61/12 NLH 8215-4J
- 10 Number of Claims: 2  
Examination not yet requested. (Total 10 pages)
- (54) Title of the Invention: POLYMER PRODUCTION PROCESS  
(21) Patent Application No.: Hei 1-202505
- 15 (22) Date of Application: August 4, 1989
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## SPECIFICATIONS

- 35 1. Title of the Invention: POLYMER PRODUCTION PROCESS
2. Scope of the Patent Claims.
- (1) A polymer production process that yields a polymer solution from which polymerization catalyst components had been removed by treating the polymerization reaction solution obtained through a ring opening metathesis polymerization of at least
- 40 one of the monomers represented by the general formula (I) described below or the

monomer with other copolymerizable monomers in the presence of a solvent and a metatheses polymerization catalyst using at least one adsorption agent selected from a group comprising activated clay, activated carbon, diatomaceous earth, activated alumina and zeolite in the presence of at least one compound represented by R-OH (R is hydrogen or a hydrocarbon group containing one to six carbon atoms).

General Formula (I)



[In the formula, A and B are hydrogen atoms or hydrocarbon groups containing one to ten carbon atoms, X and Y indicate hydrogen atoms, hydrocarbon groups containing one to ten carbon atoms, halogen atoms, hydrocarbon groups containing one to ten carbon atoms substituted with halogen atoms,  $-(CH_2)_nCOOR^1$ ,  $-(CH_2)_nOCOR^1$ ,  $-(CH_2)_nOR^1$ ,  $-(CH_2)_nCN^1$ ,  $-(CH_2)_nCONR^2R^3$ ,  $-(CH_2)_nCOOZ$ ,  $-(CH_2)_nOCOZ$ ,  $-(CH_2)_nOZ$ ,  $-(CH_2)_nW$ , or



or



composed of X and Y, at least one of X and Y is hydrogen atom or a group other than a group selected from the hydrocarbon groups {here  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrocarbon groups containing one to twenty carbon atoms, Z indicates a hydrocarbon group substituted with a halogen atom, W indicates  $SiR^5_pD_{3-p}$  ( $R^5$  is a hydrocarbon group containing one to ten carbon atoms, D indicates a halogen atom,  $-OCOR^6$  ( $R^6$  indicates a hydrocarbon group containing one to ten carbon atoms), p indicates an integer zero to three), n indicates an integer zero to ten] and m is zero or one.]

(2) The polymer production process described in Claim (1) characterized by the presence of from 0.05% by weight to 5% by weight of at least one compound

represented by R-OH in the polymerization reaction solution when the polymerization reaction solution is treated using activated clay, activated carbon, diatomaceous earth, activated alumina or zeolite.

### 3. Detailed Description of the Invention.

#### (Field of Industrial Utility)

The present invention relates to a production process for a polymer with excellent properties such as optical properties, heat resistance, weather resistance, low water absorbance, mechanical properties and the like.

#### (Conventional Technology)

Clear polymers recently have been utilized as optical materials for which optical properties are important in addition to their utility as molding materials for such applications as automobile parts, lighting equipment, electrical parts, household goods and the like in which clarity is ordinarily valued. The polymers used as optical materials not only need to be simply clear but also need to have other excellent properties such as a high degree of heat resistance, weather resistance, low water absorbance and mechanical properties.

The polymers that had been proposed as ideal optical materials up to date include a polymer obtained from tetracyclododecene type hydrocarbon compounds alone or a polymer obtained by adding hydrogen to a metathesis ring opened (co)polymer norbornene type hydrocarbon compound (Unexamined Japanese Patent Application S60-26024), a polymer obtained through metathesis ring opening polymerization of pentacyclopentadecene or a polymer obtained by hydrogen addition of the same (Unexamined Japanese Patent Application S63-145324) and a (co)polymer obtained allowing a norbornene derivative and/or tetracyclododecene derivative containing polar groups to polymerize and adding hydrogen to the polymer (Japanese Patent S57-8815 and Japanese Patent Application S62-288528).

#### (The Problems for the Invention to Solve)

The concentration of metals and other impurities in a polymer designed to be used as an optical material needs to be low in order to obtain a polymer with exceptional properties in addition to clarity as described above. For this reason, polymerization reaction solutions obtained using metathesis ring opening polymerization reaction were previously added to a large amount of poor solvent to cause the polymer to precipitate, the precipitate was further washed using the same poor solvent to remove catalyst components comprising metals and the target polymer was subsequently dried. A process in which the polymer was further dissolved in a suitable solvent and hydrogen was added was used when necessary.

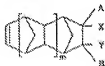
However, a large amount of the poor solvent, ordinarily at least ten fold by weight, was needed for the polymer precipitation and washing in such a process. Since the polymer concentration in a polymerization reaction solution was often about 10%, actually a poor solvent equaling at least one hundred times the weight of the polymer was needed. Therefore, the problems encountered when industrially executing the process described above were the need for a large scale solvent recovery facility and an enormous utility burden.

(Means to Solve the Problems)

The inventors conducted an intense study of the aforementioned problems. As a result, the inventors discovered that the catalyst components could be removed from polymerization reaction solutions by simply treating the reaction solution obtained after a metathesis ring opening polymerization reaction of a specific monomer with an adsorbent that is available inexpensively on industrial scale. The inventors further discovered that the presence of an appropriate amount of water in the treatment solution during such a treatment dramatically improved the removal effect. The present invention was completed based on the discoveries.

That is, the polymer production process according to the present invention yields a polymer solution from which polymerization catalyst components had been removed by treating a polymerization reaction solution obtained by metathesis ring opening polymerization of at least one monomer represented by the general formula (I) shown below or the monomer with other copolymerizable monomers in the presence of a solvent and a metathesis polymerization catalyst using at least one absorbent selected from activated clay, activated carbon, diatomaceous earth, activated alumina and zeolite in the presence of at least one compound represented by R-OH (R is hydrogen or a hydrocarbon group containing one to six carbon atoms).

General Formula (I)



[In the formula, A and B are hydrogen atoms or hydrocarbon groups containing one to ten carbon atoms, X and Y indicate hydrogen atoms, hydrocarbon groups containing one to ten carbon atoms, halogen atoms, hydrocarbon groups containing one to ten carbon

atoms substituted with halogen atoms,  $-(CH_2)_nCOOR^1$ ,  $-(CH_2)_nOCOR^1$ ,  $-(CH_2)_nOR^1$ ,  $-(CH_2)_nCN^1$ ,  $-(CH_2)_nCONR^2R^3$ ,  $-(CH_2)_nCOOZ$ ,  $-(CH_2)_nOCOZ$ ,  $-(CH_2)_nOZ$ ,  $-(CH_2)_nW$ , or



or



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composed of X and Y, at least one of X and Y is hydrogen atom or a group other than a group selected from the hydrocarbon groups {here  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are hydrocarbon groups containing one to twenty carbon atoms, Z indicates a hydrocarbon group substituted with a halogen atom, W indicates  $SiR^5_pD_{3-p}$  ( $R^5$  is a hydrocarbon group containing one to ten carbon atoms, D indicates a halogen atom,  $-OCOR^6$  ( $R^6$  indicates a hydrocarbon group containing one to ten carbon atoms), p indicates an integer zero to three), n indicates an integer zero to ten) and m is zero or one.]

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The present invention is more specifically described below.

The polymer obtained according to the process of the present invention is a polymer obtained using a ring opening polymerization of a monomer represented by the general formula (I) described above alone, a copolymer obtained using a ring opening copolymerization of said monomer with other copolymerizable monomers or a hydrogen-added polymer obtained by adding hydrogen to the polymer or the copolymer. In general, the molecular weight of such a polymer is from 20,000 to 700,000 or particularly from 30,000 to 500,000 in units of weight average molecular weight calculated in terms of polystyrene.

15

20

In a compound represented by general formula (I), A and B that are preferred for an appropriate use of the present invention are hydrogen atoms or hydrocarbon groups containing one to six carbon atoms and X and Y that are preferred are hydrogen atoms, hydrocarbon groups containing one to ten carbon atoms, halogen atoms, hydrocarbon groups containing one to ten carbon atoms substituted with halogen atoms,  $-(CH_2)_nCOOR^1$ ,  $-(CH_2)_nOCOR^1$  and  $-(CH_2)_nCN$  wherein at least one of X and Y is hydrogen atom or a group other than a group selected from the hydrocarbon groups. Furthermore, a particularly preferred compound is a compound in which A and B are both hydrogen atom or at least one of them is a hydrocarbon group containing one to three carbon atoms and at least one of X and Y is  $-(CH_2)_nCOOR^1$  or  $-(CH_2)_nOCOR^1$ .

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m is preferably one, and one to ten is a preferred number of carbon atoms in the hydrocarbon groups  $R^1$ - $R^4$ . Furthermore, a preferred number of carbon atoms is one to six, and one to three is particularly preferred.

- 5      In addition, n is preferably zero to six. From zero to two is more preferred, and zero is particularly preferred.

Of these, the following is particularly preferred.



- 10      [In the formula, R is hydrogen or an alkyl group containing one to three carbon atoms, and a methyl group is preferred.  $R^1$  is a hydrocarbon group containing one to fifteen carbon atoms.]

In addition, the monomers described above may also be used not individually but at least two of them together.

- 15      Furthermore, norbornene type compounds and cyclic olefins that can be polymerized using a metathesis polymerization catalyst and monomers that yield polymers containing carbon-carbon double bonds in the main chain may be cited as the other monomer that can copolymerize with tetracyclododecene derivatives and/or bicycloheptene derivatives.

- 20      As specific examples of other copolymerizable monomers, cyclo-olefins such as cyclopentene, cyclooctene, 1,5-cyclooctadiene, 1,5,9-cyclododecatriene and the like; polycycloalkenes such as bicyclo [2,2,1]-2-heptene, tricyclo [5,2,1,0<sup>2,6</sup>]-8-decene, tricyclo [5,2,1,0<sup>2,6</sup>]-3-decene, tricyclo [5,2,1,0<sup>2,6</sup>]-3,8-decadiene, tricyclo [6,2,1,0<sup>1,8</sup>]-9-undecene, tricyclo [6,2,1,0<sup>1,8</sup>]-4-undecene, tetracyclo [4,4,0,1<sup>2,5</sup>,1<sup>7,10</sup>]-3-dodecene, pentacyclo [6,5,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]-4-pentadecene, pentacyclo [6,5,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]-4,11-pentadecadiene, pentacyclo [6,6,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-4-hexadecene, pentacyclo [6,5,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]-11-
- 25      pentadecene and the like may be cited.

This type of other copolymerizable monomers may be used not only individually but also in a combination of at least two.

- 30      A metathesis ring opening polymerization reaction of the starting material monomers mentioned above is allowed to occur in a solvent in the presence of a metathesis polymerization catalyst ordinarily in inert atmosphere such as nitrogen, helium, argon and the like.

The temperature of the metathesis ring opening polymerization reaction is ordinarily from -30°C to 200°C. The range of from 0°C to 150°C is preferred, and the range of from 30°C to 100°C is more preferred.

- 5 The metathesis catalyst described above ordinarily is composed from a combination of the following components (a) and (b). However, the activation agents described later are sometimes also added to enhance the catalyst activity.

Component (a): At least one compound selected from the compounds of W, Mo and Re.

- 10 Component (b): At least one compound selected from the compounds of group IA, IIA, IIB, IIIA, IVA or IVB elements containing at least one bond between one said element and carbon or one said element and hydrogen.

- The compounds of W, Mo and Re suitable as the component (a) described above are halides, oxyhalides, alkoxy halides, alkoxides, carboxylate salts, (oxy)acetylacetonates, carbonyl complexes, acetonitrile complexes, hydride complexes and their derivatives or combinations thereof. However, the compounds of W and Mo, particularly their halides, oxyhalides and alkoxyhalides are preferred from the stand point of excellent polymerization activity and practicality. In addition, mixtures of at least two compounds that form the compounds described above through a reaction may also be used. These compounds may be converted into complexes using a suitable complexing agents, for example,  $P(C_6H_5)_3$ ,  $C_5H_5N$  and the like may be cited as particularly preferred compounds.
- 20

As specific preferred examples of the component (a) used,  $MoCl_5$ ,  $Mo(OC_2H_5)_2Cl_3$ ,  $WCl_6$ ,  $W(OC_2H_5)_2Cl_3$  and the like may be cited.

- 25 As specific preferred examples of the component (b) used,  $(CH_3)_3Al$ ,  $(CH_3)_3AlCl$ ,  $(CH_3)_3Al_2Cl_3$ ,  $CH_3AlCl_2$ ,  $(C_2H_5)_3Al$ ,  $(C_2H_5)_2AlCl$ ,  $(C_2H_5)_3Al_2Cl_3$ ,  $C_2H_5AlCl_2$ ,  $(C_2H_5)_2AlH$ ,  $(C_2H_5)_2AlOC_2H_5$ ,  $(C_2H_5)_2AlCN$ ,  $(C_3H_7)_3Al$ ,  $(iso-C_4H_9)_3Al$ ,  $(iso-C_4H_9)_2AlH$ ,  $(C_6H_{13})Al$ ,  $(C_8H_{17})_3Al$ ,  $(C_6H_5)_3Al$  and the like may be cited.

- The quantitative relationship between components (a) and (b) described above should be in the range of 1:1 to 1:20 or preferably from 1:2 to 1:10 for (a):(b) in terms of metal atomic ratio.
- 30

The metathesis polymerization catalyst prepared from the components (a) and (b) described above ordinarily has excellent catalytic activity in the metathesis ring opening polymerization reaction of the starting material monomer and can further be

used as a catalyst with even better activity by adding an activation agent comprising the component (c) described next.

A variety of compounds may be used as said component (c), but the compounds used particularly publicly include the following.

- 5        Boron itself, boron compounds, silicon compounds, alcohols, hydroperoxides and peroxides, water, oxygen, carbonyl compounds such as aldehydes and ketones and their oligomers and polymers, cyclic ethers, amines, azo compounds, N-nitroso compounds and compounds containing S-Cl radicals or N-Cl radicals.

- 10       The quantitative relationship between component (a) and component (b) cannot be specified indiscriminately since the relationship is extremely volatile depending on the type of component (c) added. However, the value of (c)/(a) (molar ratio) is frequently in the range of from 0.005-10, and the range of from 0.05-3.0 is preferred.

- 15       In a metathesis ring opening polymerization reaction, the molecular weight of the polymer obtained can be adjusted by changing the reaction conditions such as the type and concentration of the metathesis polymerization catalyst, polymerization temperature, type and amount of the solvent, monomer concentration and the like. However, the molecular weight of a ring opened polymer is preferably adjusted ordinarily by adding an appropriate amount of a suitable molecular weight adjusting agent.

- 20       As the molecular weight adjusting agent, a compound containing at least one carbon-carbon double bond or carbon-carbon triple bond in a molecule such as  $\alpha$ -olefins,  $\alpha,\omega$ -diolefins, acetylenes and the like or polar allyl compounds such as allyl chloride, allyl acetate, trimethylallyloxy silane and the like may be cited.

As the solvent for the polymerization reaction, the following solvent A, solvent B or mixtures thereof are used.

- 25       Solvent A comprises a mixture of solvent component (a) and solvent component (2).

- 30       As the solvent component (1), an alicyclic saturated hydrocarbon and/or aliphatic saturated hydrocarbon containing ten carbon atoms or fewer, preferably five to eight carbon atoms is used. Here, as specific examples of the alicyclic saturated hydrocarbon, cyclopentane, methyl cyclopentane, cyclohexane, methyl cyclohexane, dimethyl cyclohexane, ethyl cyclohexane, cycloheptane, decalin and the like may be cited. In addition, as specific examples of the aliphatic hydrocarbon, n-pentane, isopentane, n-hexane, n-heptane, n-octane and the like may be cited.



As the solvent component (2), dialkyl glycol ether is used. As specific examples thereof, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, triethylene glycol dimethyl ether and the like may be cited.

5 The ratio with which solvent component (1) and solvent component (2) are mixed in solvent A is ordinarily from 95:5 to 30:70 in terms of weight ratio and from 90:10 to 40:60 is preferred. When the proportion of solvent (1) is excessively large, the degree of solubility of solvent A for the polymer formed is inadequate. On the other hand, when this proportion is too small, the reaction activity of the metathesis ring opening  
10 polymerization reaction is too low and a polymer with a high degree of polymerization cannot be obtained.

Solvent B comprises only of an aromatic hydrocarbon containing six to ten carbon atoms. As specific examples thereof, benzene, toluene, xylene, ethylbenzene and the like can be cited. Not only one but two or more aromatic hydrocarbons may also  
15 be used.

The monomer concentration in a metathesis ring opening polymerization reaction conducted in the solvent described above is ordinarily from 10% by weight to 40% by weight.

Upon completion of the metathesis ring opening polymerization reaction, a  
20 catalyst removal aid may also be added to the polymerization reaction solution obtained.

As the catalyst removal aid, organic amines such as triethanolamine, diethanolamine, monoethanolamine, triethylamine, diethylamine, tri-propylamine, tri-butylamine, di-butylamine, ethylene diamine, hexamethylene diamine, poly(ethylene diamine), pyridine, tetra-methyl ammonium hydroxide and the like; inorganic alkalis such  
25 as sodium hydroxide, potassium hydroxide, sodium carbonate and the like may be cited.

The amount added of the catalyst removal aid varies according to the type. However, from one mole to one thousand moles per mole of the metathesis polymerization catalyst used is ordinarily used, and from five moles to one hundred moles is preferred.

30 In the present invention, the polymerization reaction solution obtained in the manner described above or a diluted solution thereof is treated using at least one adsorbent selected from activated clay, activated carbon, diatomaceous earth, activated alumina and zeolite.

The treatment method used varies with the shape of the adsorbent. When a powder is used, the powder is ordinarily added to a polymerization reaction solution, the mixture is agitated and the adsorbent is subsequently separated using an operation such as filtration or centrifugal separation to yield a polymer solution. In addition, when  
5 adsorbent granules are used, a packing method that is a flow through type continuous treatment may be conducted although the aforementioned treatment process may also be used.

The amount of an adsorbent used varies with the type and shape as well as the amount of the catalyst used in the polymerization, solvent type and the like. The amount  
10 per polymer in the polymerization reaction solution is ordinarily from 0.2% by weight to 200% by weight, and from 1% by weight to 100% by weight is preferred. The catalyst removal effect is inadequate when the amount used is less than 0.2% by weight, and the economic demerit is too great when the amount used exceeds 200% by weight. In addition, the amount of an adsorbent used in a packed method is determined by LHSV,  
15 catalyst life and the like and is difficult to make a sweeping determination. However, the aforementioned amount should be used as a gauge.

The conditions such as temperature, time and the like for the treatment are not particularly restricted, and industrial conditions suited are selected.

Next, the presence of a compound represented by R-OH is another significant  
20 feature of the present invention. The presence can greatly improve the catalyst removal effect and, as a result, can greatly reduce the amount of adsorbent used to yield an industrially advantageous treatment process.

The R-OH compound contains R that is hydrogen or a hydrocarbon group containing one to six or preferably one to four carbon atoms, and at least one of them is  
25 used. Of the R-OH compounds, those in which R is hydrogen, that is, water is preferred. In addition, R is preferably a hydrocarbon group when the solvent used in the polymerization reaction is difficult to dissolve in water. The effect is excellent even when water alone is added, but a combined use of the compounds described above (alcohols) and water is particularly preferred.

30 The water/alcohol mix ratio is not particularly restricted and can be optionally selected.

A treatment process in which an adsorbent is impregnated first in an R-OH compound is ordinarily used, but a process in which an R-OH compound is added to the polymerization reaction solution may also be used.

The amount of the R-OH compound present varies according to the type and amount of the adsorbent as well as the solvent type and the like of the polymerization reaction solution. However, the amount used is ordinarily from 0.05% by weight to 5% by weight per polymerization reaction solution or a diluted solution thereof, and from 0.1% by weight to 4% by weight is preferred. The presence is less effective when the amount is greater or smaller than the range. When an appropriate amount of R-OH compound is present, the adsorbent amount used can be reduced to 1/10 or less depending on the adsorbent type.

A hydrogen added polymer with improved thermal stability and weather resistance can be obtained by further adding hydrogen when necessary to the polymer solution from which the polymerization catalyst components had been removed in the manner described above.

The hydrogen addition reaction is conducted by adding a hydrogen addition catalyst to a polymer solution and using the action of hydrogen gas at from ambient pressure to three hundred atmospheric pressure or preferably from two atmospheric pressure to one hundred fifty atmospheric pressure at from 0°C to 200°C or preferably from 20°C to 180°C.

As the hydrogen addition catalyst, those that are ordinarily used in the hydrogen addition reaction of olefinic compounds may be used. As the hydrogen addition catalyst, heterogeneous catalysts and homogeneous catalysts are well known.

As the heterogeneous catalyst, a solid catalyst obtained by supporting a catalytic substance such as palladium, platinum, nickel, rhodium, ruthenium and the like on individual materials such as carbon, silica, alumina, titania and the like may be cited.

In addition, as the homogeneous catalyst, nickel naphthinate/triethyl aluminum, nickel acetyl acetonate/triethyl aluminum, cobalt octinate/n-butyl lithium, titanocene dichloride/diethyl aluminum monochloride, rhodium such as rhodium acetate, chlorotris(triphenyl phosphine) rhodium and the like may be cited.

The hydrogen addition reaction is preferably conducted so that the hydrogen addition rate in the hydrogen added polymer obtained is at least 50%, preferably at least 70% and more preferably at least 80%. The reason for the preference is based on the fact that the greater the hydrogen addition rate, the better the thermal stability and weather resistance in general. For example, a hydrogen added polymer with less than 50% hydrogen addition rate risks being impractical due to lack of thermal stability and

weather resistance. Simultaneously, a hydrogen added polymer with a hydrogen addition rate of 100% is sometimes required depending on the application.

A post treatment according to the catalyst type is conducted on a polymer solution after a hydrogen addition reaction. A hydrogen added polymer is obtained by removing the solvent using a device such as a concentrator, evaporator, ventruder [transliteration] and the like after removing the catalyst using filtration and the like when a solid catalyst is used. In addition, a hydrogen-added polymer can also be obtained using a process such as steam stripping and coagulation in an ordinary poor solvent.

In a process of the present invention, various additives, for example an oxidation inhibitor, may be added as needed upon completion of the metathesis ring opening polymerization reaction or after a treatment using an adsorbent and upon completion of a hydrogen addition reaction.

As examples of the oxidation inhibitor, 2,6-di-t-butyl-4-methylphenol, 2,2'-dioxy-3,3'-di-t-butyl-5,5'-dimethyl diphenyl methane, phenyl- $\beta$ -naphthylamine, pentaerythritol-tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate], tris(2,4-di-t-butylphenyl) phosphite, bis-(2,6-di-t-butyl-4-methylphenyl) pentaerythritol diphosphite and the like may be cited.

The clear polymer produced according to the process of the present invention is of extremely high purity and has many particularly excellent properties such as optical properties, heat resistance, weather resistance, mechanical properties and the like. The clear polymer can be used in general molding materials utilizing these properties but also can ideally be used in optical materials such as optical video disks, audio disks, document file disks, memory disks, camera lens, laser beam lens and the like.

In addition, the polymer produced using the present invention can yield properties that are insufficient in individual resins when blended with existing resin materials, for example, styrene type resins, acrylic resins, polyester resins, polyamide resins, polycarbonate resins, poly(phenylene oxide) resins, poly(phenylene sulfide) resins, poly(ether sulfone) resins, polysulfone resins, polyimide resins, polybutadiene resins, ABS resins, AES resins, hydrogenated styrene-butadiene block copolymers and the like.

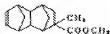
#### [Examples]

Examples of the present invention are explained below, but the present invention is not restricted by the examples.

### Example 1

#### <Sample Preparation>

Eight kilograms (34.5 moles) of the monomer (8-methyl-8-carboxymethyl tetracyclo[4,4,0,1<sup>2,5</sup>,1<sup>7,10</sup>]-3-dodecene) represented by the structural formula



24.0 kg of a solvent (henceforth referred to as solvent A<sup>Ⓢ</sup>) that is a 8:2 mixture of cyclohexane with the moisture removed and ethylene glycol dimethyl ether and 580 g (6.9 moles) of 1-hexene that is a molecular weight adjustment agent were added to a 50 liter reactor that had been purged with nitrogen gas. To this, 140 g of an ethylene glycol dimethyl ether solution of tungsten hexachloride with a concentration of 0.05 mole/liter, 140 g of a cyclohexane solution of diethyl aluminum chloride with a concentration of 0.96 mole/liter and 30 g of an ethylene glycol dimethyl ether solution of paraldehyde with a concentration of 0.2 mole/liter were added as metathesis polymerization catalysts, and a polymerization reaction was allowed to occur for three hours at 80°C. The monomer conversion rate in this polymerization reaction was 98.0% based on the gas chromatographic analysis of the polymerization reaction solution obtained.

The polymerization reaction solution obtained was diluted using solvent A<sup>Ⓢ</sup>, and the polymer concentration was adjusted to 10% by weight. The prepared solution was referred to as sample S. The water content in the sample S was 0.02% by weight or less. In addition, the tungsten and aluminum contents in the sample S were analyzed using fluorescent X ray method and atomic light absorption method and were 180 ppm and 600 ppm, respectively, per polymer that were nearly the theoretical values for the polymerization catalysts used. Henceforth, the sample S was subjected to adsorption treatment experiments.

#### <Treatment Experiments>

A material obtained by impregnating 100 g of sample S and 0.5 g of activated clay (trade name Galeon Earth V2) used as the adsorbent in 0.5 g of water was added to a 200 ml flask equipped with an agitator. The mixture was agitated for two hours at room temperature. Next, said treatment solution was placed in a centrifugal separator to separate the adsorbent, and a polymer solution was obtained as a clear supernatant solution. The residual tungsten and aluminum in the polymer solution was analyzed. As shown in Table 1, the concentrations were 7 ppm and 3 ppm per polymer, and the removal rates were 96% and >99%, respectively.

## Examples 2-6

The same treatment experiments described in Example 1 were conducted using sample S by changing the type and amount of the adsorbent. The results were shown in Table 1.

## 5 Examples 7

One gram of water was first added to 100 g of sample S to dissolve the sample. One gram of activated clay (10% by weight based on the polymer) was added, and the same treatment experiment conducted in Example 1 was conducted. As demonstrated by the results that were shown in Table 1, the catalyst removal rate was equivalent to  
10 that achieved in Example 2 in which the same amount of an adsorbent was added. The same effect was realized even when a sample was dissolved first without impregnating the adsorbent in water.

Based on the examples presented above, polymerization catalyst components could be removed from a metatheses ring opening polymerization reaction solution  
15 obtained using a specific monomer according to a process of the present invention by using a treatment involving an industrially inexpensive adsorbent. In addition, the amount used clearly could be a small amount.

## Comparative Example 1

Untreated sample S.

## 20 Comparative Example 2

One hundred grams of sample S and 2 g (20% by weight based on the polymer) of activated clay (trade name, Galeon Earth V2) as the adsorbent were added to a 200 ml flask equipped with an agitator. The mixture was agitated for two hours at room  
25 temperature. Next, said treatment solution was placed in a centrifugal separator to separate the adsorbent. A clear polymer solution was obtained as the supernatant solution. The residual tungsten and aluminum amounts in the polymer solution were analyzed. The results indicated, as shown in Table 1, that the residual amounts were 30 ppm and 50 ppm and the removal rates were 83% and 92%, respectively.

## Comparative Examples 3-6

30 The same treatment experiments described in Example 1 were conducted using sample S by changing the type and amount of the adsorbent. The results were shown in Table 1.

Table 1

	Adsorbent		Water		Treatment results			
	Type (trade name)	Am. added	Water addition	Am. of water in treatment sol'n (wt.%)	W		Al	
		Am. per polymer (wt.%)			Am. per polymer (ppm)	Removal rate (%)	Am. per polymer (ppm)	Removal rate (%)
Example 1	Activated clay (Galeon Earth V2)	5	Added	0.5	7	96	3	>99 (99.5)
Example 2	"	10	"	1.0	4	98	2	>99 (99.7)
Example 3	Activated carbon	20	"	0.5	4	98	3	>99 (99.5)
Example 4	Diatomaceous earth	20	"	0.5	39	78	55	91
Example 5	Activated alumina	20	"	0.5	7	96	6	99
Example 6	Zeolite (MS-13X)	20	"	0.5	11	94	8	99
Example 7	Activated clay (Galeon Earth V2)	10	"	1.0	5	97	3	>99 (99.5)
Comp. Ex. 1	--	0	None added	0.05 or less	180	0	600	0
Comp. Ex. 2	Activated clay (Galeon Earth V2)	20	"	"	30	83	50	92
Comp. Ex. 3	Activated carbon	20	"	"	100	44	250	58
Comp. Ex. 4	Diatomaceous earth	100	"	"	130	28	350	42
Comp. Ex. 5	Activated alumina	100	"	"	120	33	300	50
Comp. Ex. 6	Zeolite (MS-13X)	100	"	"	140	22	320	47

Example 8

One hundred grams of sample S and one gram of activated clay impregnated with 0.5 g of methanol was added, and the same treatment experiment described in Example 1 was conducted. The results are shown in Table 2.

5 Example 9

A treatment experiment was conducted by replacing methanol with ethanol in Example 8. The results are shown in Table 2.

Example 10

10 A treatment experiment was conducted by using water and methanol in combination in Example 8. The results are shown in Table 2.

Example 11

In the sample preparation process of Example 1, dried toluene was used as the solvent in place of solvent A<sup>①</sup> when conducting the polymerization. The monomer conversion rate in the polymerization reaction was the same 98.0% observed in

15 Example 1.

The polymerization reaction solution obtained here was diluted with toluene, and the polymer concentration was adjusted to 10% by weight. The solution prepared was referred to as sample S<sub>2</sub>.

20 The water fraction in the sample S<sub>2</sub> was 0.02% by weight or less, and the tungsten and aluminum contents were 180 ppm and 600 ppm, respectively, per polymer.

The same treatment experiment of Example 1 was conducted by adding one hundred grams of sample S<sub>2</sub> and one gram of activated clay that was impregnated with 1.5 g of methanol. The results are shown in Table 2.

Example 12

25 Sample S<sub>2</sub> was used, and a treatment experiment was conducted using a combination of water and methanol. The results are shown in Table 2.



Table 2

	Adsorbent						Treatment results			
	Type (trade name)	Am. added	Water		Alcohol		W		Al	
		Amount per polymer (wt%)	Water addition or no water addition	Water content in the treated solution (wt%)	Type	Contents in a treatment solution (wt%)	Am. per polymer (ppm)	Removal rate (%)	Am. per polymer (ppm)	Removal rate (%)
Example 8	Activated clay (Galeon Earth V2)	10	No water added	0.05 or less	Methanol	0.5	27	85	45	93
Example 9	"	10	"	"	Ethanol	0.5	36	80	55	91
Example 10	"	10	Water added	0.5	Methanol	0.5	18	90	20	97
Example 11	"	10	No water added	0.05 or less	"	1.5	32	82	50	92
Example 12	"	10	Water added	0.5	"	1.0	25	86	44	93

[Advantages of the Invention]

A desired clear resin can be produced extremely advantageously according to the process of the present invention when polymerization catalyst components are removed from a metathesis ring opening polymerization reaction solution of a specific cyclic monomer by simply treating the solution using an inexpensive adsorbent without using a large amount of alcohol in the purification step as previously was.

In addition, the polymerization catalyst component removal effect can be extensively improved and the amount of the adsorbent used can be greatly reduced by having an appropriate amount of the compound represented by R-OH present in the treatment solution particularly when the adsorbent is used for the treatment making the process of the present invention extremely advantageous industrially.

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